PRODUCT ANALYSIS FROM DIRECT LIQUEFACTION OF SEVERAL
HIGH-MOISTURE BIOMASS FEEDSTOCKS

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PROCESS RESEARCH IN DIRECT LIQUEFACTION OF BIOMASS

Significant progress has been made over the past fifteen years toward the development of processes for direct production of liquid fuels from biomass. Process research has generally progressed along two lines -- flash pyrolysis and high-pressure processing. Extensive analysis of the liquid products from these two types of processes has demonstrated the significant process-related differences in product composition. However, the effect of feedstock has received a lesser degree of attention.

Liquefaction Processes

Two generalized categories of direct liquefaction processes can be identi-fied.(1) The first, flash pyrolysis, is characterized by a short residence time in the reactor (~1 second) at relatively high temperature (450-500°C) in order to obtain maximum yield of liquid product. The second, high-pressure processing, is usually performed at lower temperature (300-400°C) and longer residence time (0.2-1.0 hr). A typical operating pressure is 200 atm and often reducing gas and/or a catalyst is included in the process. The differences in processing conditions result in significant differences in product yield and product composition.

Product Analyses

Product analysis in support of the process development research in biomass direct liquefaction began at rudimentary level of determining solvent-soluble portions of the product. Analysis was soon extended to elemental analyses and proximate analyses, such as ash and moisture. Later, spectrometric analyses were performed followed by detailed chemical analyses used in conjunction with chromato-graphic separation techniques.

At all stages of development, the significant differences in composition between the products of flash pyrolysis and high-pressure processing have been evident. While polar solvents are most effective for both products, less polar solvents such as methylene chloride and even benzene and toluene have been used as extrac-tants for high-pressure product oils. Comparative analysis has demonstrated the higher oxygen content and higher dissolved water content in the flash pyrolysis oils. Detailed analyses with spectrometric and chromatographic methods have added supporting evidence to these findings.

Variations in Product Due to Feedstock

While process-related differences in product composition have been evident, extensive study of the effect of feedstock on product composition has never been undertaken. Some limited comparative tests can be gleaned from the literature; however, most process research in direct liquefaction of biomass has been performed with woods of various species. Table 1 provides some of the results available in the literature for non-woody feedstocks. Significant differences in heteroatom content are evident, but only limited chemical analysis is available in most cases.

TABLE 1. Product Analyses from Liquefaction Tests with Various Biomasses

Feedstock	Temp. °C	Pressure psig	C	H	N	O	S	H/C
					percent			
High-Pressure Processes								
(2) newsprint	250	2,000	71.7	7.3	<0.3	~20.6	<0.1	1.21
(2) pine needles & twigs	250	2,000	72.2	8.7	1.05	18.0	0.10	1.43
(2) sewage sludge	250	2,000	77.0	10.7	2.80	8.8	0.64	1.65
(3) cellulose	250	2,000	72.4	7.0	.004	20.4	0.2	1.15
(3) sucrose	350	4,000	75.2	9.1	--	15.7	--	1.44
(4) municipal refuse	380	5,000	79.8	10.4	3.0	6.8	0.05	1.55
(4) manure	380	4,500∞	80.4	9.4	3.0	6.9	0.26	1.39
(5) microalgae	400	4,000∞	*81.2	8.6	5.4	3.5	--	1.26
Flash Pyrolysis								
(6) aspen	450	0	53.8	6.7	--	39.3	--	1.48
(7) sewage sludge	450	0	69.4	10.2	5.8	14.5	--	1.75
(8) poplar	500	0	49.8	7.3	0.0	42.8	0.0	1.74
(8) peat	520	0	67.1	9.0	3.4	20.3	0.1	1.59

∞ estimate
* the microalgae analysis was calculated from the analysis of product fractions
   (oil and asphaltene) and the product distribution

The researchers at the Pittsburgh Energy Research Center (2,3,4) steadfastly maintained in their pioneering work that their oil products obtained from cellulosic wastes were paraffinic and cycloparaffinic in nature. They reported the presence of carbonyl and carboxyl functional groups but maintained that there was essentially no aromatic material produced except at higher temperature (then only in very small amounts). These conclusions were based on infrared and mass spectral analysis.(2) Later analysis of the sucrose-derived oil (3) included proton nuclear magnetic resonance spectral evaluation but resulted in the same conclusion. Most of the hydrogen was in methylene or methyl groups and about 4 percent was unsaturated but probably olefinic and not aromatic. Some ether linkages were also reported present in the sucrose-derived oil. Mass spectral analysis of the municipal refuse-derived oil (4) identified only two long chain fatty acids with certainty; however, not more than traces of aromatics were determined to be present. The manure-derived oil was found to be largely alicyclic hydrocarbon but contained heterocyclic nitrogen and alkyl phenolics.(4) These claims of the saturated hydrocarbon nature of the oil products are at odds with the reported elemental analyses (see Table 1). The low hydrogen to carbon ratios dictate that the oil products must contain a large fraction of aromatic or, at least, highly unsaturated compounds.

An algae-derived oil was reported to be principally n-paraffins and olefins with oxygen- and nitrogen-containing straight-chain hydrocarbons.(5) Polar compounds were reported to comprise 50-60 percent of the oil. Unfortunately, there is no indication of the type of analysis performed or detailed results of any kind; therefore, it is difficult to evaluate the veracity of these reported results.

The comparison of the peat and wood flash pyrolysis products is a good example of the effect of feedstock on product oil composition.(8) The poplar oil typically was composed of phenolic, ketone and furan compounds with a substantial fraction of low molecular weight organic acids. The main components of the peat oil were hydrocarbons, mostly straight chain olefins. Minor quantities of ketones were

noted but no acids, aldehydes or furans were identified by mass spectrometry. Phenols were also present in significant quantities.

A significant effort in comparing feedstock effects on product oil composition was reported by Russell et al.(9) Unfortunately, this effort did not include ultimate analysis of the oils for comparison. The report contains qualitative analysis by gas chromatography/mass spectrometry of five product oils derived from cellulose, hops field residue, softwood tree branches, peat, and sewage sludge. Phenols were a major component group for all feedstocks. Ketones and furans were also common. Hydrocarbons, aromatic and otherwise, were also identified primarily in the cellulose and softwood products. Nitrogen-containing products were absent from the cellulose and softwood products but could be found in the peat and sewage sludge-derived oils.

All of the above accounts can be contrasted with the large amount of analytical work on the chemical composition of wood-derived direct liquefaction products which has been reported over the past several years.(8,10-16) In all cases the majority of the product oils have been identified as phenolic with only minor amounts of pure hydrocarbon reported.

LIQUEFACTION EXPERIMENTS WITH MOIST BIOMASS

At Pacific Northwest Laboratory we have been testing the use of high-moisture biomass (marine and fresh-water biomass, post-harvest field residues and food processing wastes) in a thermochemical conversion system to produce useful fuels. Although the main focus of the work (17) has been gasification (catalytic production of methane) we have also performed a limited number of tests under high-pressure liquefaction conditions.

Feedstock Description

Five high-moisture biomass feedstocks were tested in these liquefaction experiments. They are characterized as follows:

Kelp - The sample used was a freshly harvested macrocystis kelp from Pacific Ocean seabeds off the southern California coast (El Capitan Beach, Santa Barbara Channel). It was packed in ice and flown to our laboratory where it was frozen in a polyethylene bag until used.

Water Hyacinth - Uprooted samples of hyacinths were recovered from the primary treatment lagoon at the Reedy Creek experimental sewage treatment facility near Orlando, Florida. The sample was packed in ice and flown to our laboratory where it was frozen in a polyethylene bag until used.

Spent Grain - The grain sample used was the residue following malting barley and water extraction of the sugars prior to fermentation. The sample was obtained from the Blitz-Weinhard Brewery in Portland, Oregon and was transported to our laboratory where it was frozen until used.

Napier Grass - Napier grass was collected after harvest by University of Florida researchers. The sample was bagged and shipped in a refrigerated container to our laboratory where it was stored in a freezer until used.

Sorghum - Grain sorghum was collected after the harvest of the grain by the University of Florida. The sample containing stems, stalks, and leaves was bagged and shipped in a refrigerated container to our laboratory where it was stored in a freezer until used.

Ultimate analysis, moisture contents and energy contents for the five feedstocks
are provided in Table 2.

TABLE 2. Analysis of Moist-Biomass Feedstocks

	C	H	N	O	Ash	Moisture	HHV*
	percent, dried basis					percent	BTU/lb
Kelp	26.9	4.0	1.2	30.2	38.4	88.9	7150
Water Hyacinth	43.0	5.8	5.6	29.5	15.3	94.9	7730
Spent Grain	48.6	6.8	3.4	35.3	3.4	80.5	9160
Napier Grass	44.5	5.9	<0.1	41.9	5.7	84.4	7870
Sorghum	44.7	5.8	0.2	37.5	7.9	77.0	8046

*HHV = higher heating value of dried biomass

Reactor Conditions

The experiments were performed batchwise in a one-liter, stirred autoclave.
Approximately 300 g of moist-biomass was charged to the autoclave in a stainless
steel liner. Sodium carbonate was added to the feedstock (approximately 0.1 g/g
dry biomass) except in the case of kelp which already contains a high level of
alkali as part of its chemical makeup.

The autoclave was then sealed, purged with nitrogen and then pressurized with
carbon monoxide (approximately 50 atm). The reactor was heated to 350°C (approxi-
mately 30 minutes from 200° to 350°C) and held at that temperature for 30 minutes.
The pressure within the autoclave at temperature typically increased from 270 atm
to 340 atm over the period of the experiment. At the end of the allotted time
cooling water was flushed through our internal cooling coil which brought the reactor
temperature down to 200°C within 5 minutes.

Product Recovery and Analysis

After the autoclave had cooled completely, the gas product was vented. The
typical gas composition included nearly equal parts of hydrogen and carbon dioxide
with a 10-15 percent residual amount of carbon monoxide and minor amounts of
hydrocarbons. [These results suggest a strong water-gas shift reaction as cata-
lyzed by the sodium carbonate base.(18)] The autoclave was then opened and the
two-phase liquid product was collected. The autoclave was rinsed with acetone and
the resulting wash solution filtered. The liquid product was acidified to pH 2
with dilute HCl and then extracted with methylene chloride.

The soluble and insoluble products were analyzed for elemental content of
carbon, hydrogen, nitrogen and oxygen with Perkin-Elmer 240 series instruments.
The methylene chloride soluble oil product was also analyzed as a methylene chloride
solution on a gas chromatograph equipped with a mass selective detector for
qualitative analysis and a similar gas chromatograph equipped with a flame ionization
detector for quantitative analysis. Identification of compounds was made by
comparison of mass spectra with library listings of known compounds in conjunction
with a comparison of chromatograph column residence time with similar known
compounds. Quantitative analysis was based on a known amount of internal standard
(trans-decahydronaphthalene) with detector response factors determined for various
functional group types. Quantitation is estimated at within ± 20 percent. DB-5
capillary columns are used in both chromatographs.

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LIQUEFACTION RESULTS AND PRODUCT DESCRIPTION

Liquefaction Experimental Results

Results from the liquefaction experiments with the five moist-biomass feedstocks are given in Table 3. The oil yield is based on the combined mass of acetone- and methylene-chloride soluble oils as a percent of the mass of dried feedstock calculated to an ash-free basis. The product oil elemental analysis is the calculated composite analysis for the combined acetone- and methylene chloride-soluble oils.

TABLE 3. Experimental Results for Liquefaction Experiments

	Oil Yield	C	H	N	O	H/C
	percent	combined oil analyses
Kelp	19.2	76.7	8.9	3.5	9.9	1.38
Water Hyacinth	26.0	76.3	9.9	3.3	10.5	1.54
Spent Grain	34.7	75.2	10.2	3.8	10.8	1.61
Napier Grass	34.4	74.5	8.5	0.4	16.7	1.36
Sorghum	26.6	75.9	8.7	1.7	13.7	1.36

The test results in Table 3 demonstrate oil product yields for liquefaction of the moist-biomass feedstocks at levels comparable to wood liquefaction. Reported yields for wood liquefaction in aqueous slurries, such as the LBL process,(19) have typically been in the 25 to 30 weight percent range. The quality of the moist-biomass liquefaction products fall in a general range which is also similar to reports for wood liquefaction products. However, certain examples of moist-biomass product oils appear to have elemental compositions suggesting higher quality products. Especially interesting are the high hydrogen to carbon ratios for the spent grain and water hyacinth products and the relatively low oxygen contents of the spent grain, water hyacinth and kelp products. A significant difference from wood-derived oils is the high nitrogen content in the oils from spent grain and aquatic biomasses.

Product Analysis Details

The detailed chemical analysis of the five moist-biomass derived oils by gas chromatography and mass spectrometry helps to better define the differences in oil composition. Over 190 different compounds and isomers were identified in the five oils. In order to better understand this large amount of information the components have been grouped by chemical functionality and these groups are listed in Table 4.

The compound groups consist of the following types of compounds:

esters/aldehydes/alcohols - four to six carbon oxygenates
cyclic ketones - five and six carbon rings, many unsaturated, most alkylated
furans - dihydrofuranones, hydroxymethyltetrahydrofuran
phenols - phenol and alkylated (up to five carbons) phenols
methoxyphenols - mono- and dimethoxyphenols and alkylated forms
benzenediols - dihydroxybenzenes and alkylated (up to five carbons) forms
naphthols - naphthols and methylated naphthols
aromatic oxygenates - bismethylguaiacol(?), phenylphenols, benzodioxin(?)
cyclic hydrocarbons-alkylcyclopentenes, alkylbenzenes(?), alkylindans, phenanthrene
long-chain hydrocarbons - C_{14} to C_{27} n-alkanes and olefins
fatty acids - C_{12} to C_{20} saturated and unsaturated acids
nitrogen cyclics-alkylpyrrolidinones, alkylaziridines(?), alkylpyrroles, alkylindoles
amines/amides - C_8 to C_{22} amines/amides(?)

TABLE 4. Chemical Functional Groups in Moist-Biomass Oil Products*

Compound Group	Kelp	Water Hyacinth	Spent Grain	Napier Grass	Sorghum
esters/aldehydes/alcohols	0 (1)	0 (0)	0 (1)	3 (4)	0 (0)
cyclic ketones	8 (13)	3 (9)	7 (10)	20 (25)	6 (12)
furans	0 (0)	1 (1)	4 (3)	2 (3)	2 (3)
phenols	11 (9)	22 (18)	26 (15)	35 (24)	21 (14)
methoxy phenols	3 (3)	3 (2)	3 (1)	5 (5)	10 (5)
benzenediols	11 (2)	6 (4)	0 (0)	6 (6)	25 (11)
naphthols	9 (5)	2 (3)	0 (0)	5 (9)	9 (6)
aromatic oxygenates	1 (2)	3 (3)	6 (2)	4 (5)	2 (2)
cyclic hydrocarbons	21 (15)	12 (18)	7 (9)	16 (24)	16 (19)
long-chain hydrocarbons	6 (3)	16 (15)	5 (4)	3 (9)	4 (4)
fatty acids	11 (3)	8 (7)	8 (4)	1 (2)	5 (4)
nitrogen cyclics	17 (11)	17 (11)	19 (7)	0 (0)	0 (0)
amines/amides	3 (1)	6 (3)	15 (7)	0 (0)	0 (0)
percent identified	10.3	17.8	14.2	20.4	17.8

* tabular listing is the mass percent of identified oil components in each compound
  group; the number in parentheses is the number of individual compounds and
  isomers in each compound group

Comparison to Earlier Results

These results verify that the carbohydrate structures found in biomass can be converted thermochemically to a mixture of primarily phenolic compounds. Hydrocarbons are not predominant yet they may survive the processing in a significant yield given an appropriate feedstock. Cyclic ketones are the other major component group which can be identified by GC/MS. Low molecular weight oxygenates and furans are minimized by the addition of base to the reaction medium as has been demonstrated by other researchers.[20]

The product compositions of the napier grass and sorghum-derived product oils shown many similarities to wood-derived oils. In comparing with high-pressure processed oil from Douglas fir the same groups of cyclic ketones, phenols, naphthols, and dihydroxybenzenes dominate. The traces of hydrocarbon in the sorghum and napier grass oils are significantly different from the Douglas fir and are apparently feedstock related. Nitrogen-containing compounds were not found in either the Douglas fir oils or the sorghum or napier grass oils reported here.

The large fraction of nitrogen-containing cyclic compounds is the distinguishing factor between the hyacinth, kelp and grain oils when compared to earlier wood oil analyses. Similar compounds were found earlier in peat and sewage sludge oils.[9] Our results now extend this trend to high protein feedstocks and green,

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aquatic plants. It is obvious that a strong correlation exists between nitrogen content of the feedstock and the amount of nitrogen incorporated into the product oil. High-pressure liquefaction even with a reducing gas environment and alkaline catalysis cannot effect a preferential denitrogenation reaction. Substantial amounts of nitrogen are condensed into cyclic systems which remain in the oil product.

Utilization of Oil Products from Moist Biomass

The oil products from these high-moisture biomasses have properties similar to the more widely studied wood-derived oils. The numerous applications of wood-derived oil have been discussed by others (10a, 20). The moist-biomass oils should be amenable to the same types of applications. In addition, the nitrogen-containing compounds may be useful as chemical commodities. Indoles in particular may be recoverable for use as fragrances or flavors. The hydrocarbon component in the oils may facilitate the direct use of these oils as fuels.

The nitrogen-containing components in some of the moist-biomass oils is a source of concern when considering their use as fuels. Direct utilization of these oils would certainly lead to higher levels of emission of NO_x. The nitrogen-containing components have also been indicated as a source of fuel instability during storage and as cancer-causing agents in various chemical forms. Hydrotreating of these oil products to remove the nitrogen is a possible means of upgrading the products. However, hydrodenitrogenation of the heterocyclic compounds is a difficult and costly procedure compared to hydrodeoxygenation of the phenolics, which would also be accomplished in a hydrotreating type of oil upgrading.

Implications for Future Research

The high-moisture biomass feedstocks can be a source of useful liquid fuel products. The use of the high-moisture biomasses in high-pressure processing will allow their utilization in a thermochemical process without prior drying. Other research on the use of these feedstocks in high-pressure gasification has suggested the feasibility of feeding these materials as a slurry following maceration.(17) This same type of feeding should allow direct utilization of high-moisture biomass in high-pressure liquefaction processing. Experimental verification of this type of continuous processing needs to be undertaken.

The use of the nitrogen-containing feedstocks will lead to production of a nitrogen-containing oil product. Direct utilization of this oil product as a fuel will likely require development of appropriate emission control techniques in order to maintain air quality. Alternately, nitrogen-containing components can be removed from the oil product for use as specialty chemicals or by hydrotreating. Further development of hydrotreating technology specific to these oils may be necessary in order to process the heterocyclic nitrogen-containing compounds which require extensive processing in order to effect nitrogen removal.

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